

## REACTIONS OF DIBORON TETRAHALIDES WITH HALOOLEFINS. FORMATION OF POLY(DIHALOBORYL)ETHANES

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### SUMMARY

Tetrachlorodiborane(4) reacts with vinyl chloride in 2/1 ratio to yield 1,1,2-tris-(dichloroboryl)ethane and boron trichloride. The reaction appears to be general for a variety of haloolefins. Both  $B_2Cl_4$  and  $B_2F_4$  react similarly with haloethylenes containing halogens heavier than the halogen on the diboron moiety. Evidence has been obtained for a reaction sequence involving addition of  $B_2X_4$  to the haloolefin, elimination of trihaloborane, and subsequent addition of  $B_2X_4$  to the resulting vinyl-dihaloborane.

### INTRODUCTION

The well-known addition of diboron tetrahalides to olefins to form vicinal bis(dihaloboryl)alkanes is a characteristic reaction of these subvalent boron derivatives. Facile addition to a wide range of unsaturated organic and organometallic systems<sup>1-8</sup> has been reported. Qualitative and semi-quantitative kinetic data suggest that the rate of the reaction is quite sensitive to structure; addition to terminal olefins, for example, is more rapid than to internal olefins, while ethylene reacts most rapidly of all the olefins investigated<sup>2,9</sup>.

It is generally agreed that the presence of electron-withdrawing substituents on an olefinic carbon greatly reduces the reactivity of the olefin toward  $B_2Cl_4$ . In their investigations of the addition reaction, Schlesinger and his co-workers<sup>2</sup> noted that no isolable addition product was obtained from  $B_2Cl_4$  with vinyl chloride, 1,2-dichloroethylene, vinyl fluoride, 1,1-difluoroethylene or tetrafluoroethylene at room temperature or slightly above. Other workers<sup>3</sup> found that interaction of the subhalide with trichloroethylene gave mixtures from which the olefin could be quantitatively recovered by addition of ammonia. Thus, it is commonly asserted<sup>9-11</sup> that the addition reaction does not occur with olefins containing halogen on an unsaturated carbon atom.

Several groups<sup>2,3,8</sup> have noted, however, that in the presence of haloolefins  $B_2Cl_4$  is apparently stabilized against disproportionation to  $BCl_3$  and the highly colored subchlorides that form readily when the tetrahalide is stored at 0° or above.

Formation in such systems of a complex involving the olefinic  $\pi$ -system and the vacant or partially vacant  $p$ -orbitals of the boron compound has been suggested<sup>9</sup> as the basis of the stabilization observed.

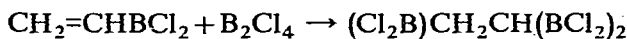
In an earlier study<sup>8</sup> from one of these laboratories dealing with the addition of boron subhalides to vinylmetallic derivatives, we obtained evidence for a slow reaction between  $B_2Cl_4$  and 2-chlorovinylchloroborane, leading to the formation of saturated organoboron products. Although this proved to be more complex than a simple addition to the double bond, the indication of an authentic reaction between  $B_2Cl_4$  and a chloroethylene led us to reexamine the interactions in  $B_2Cl_4$ -haloolefin systems\*.

## RESULTS AND DISCUSSION

In agreement with the results of earlier workers<sup>2,3</sup>, we observed a marked inhibition of the formation of colored disproportionation products in mixtures of  $B_2Cl_4$  with haloolefins. That this is not merely a dilution effect is clearly indicated by experiments using *n*-hexane and ethyl chloride as inert diluents, where significant amounts of red precipitates formed at 25°, even with relatively slight (8–10%) decomposition of  $B_2Cl_4$ . In this sense, the "stabilization" of  $B_2Cl_4$  by haloolefins appears to be a real phenomenon. In the case of vinyl chloride, the "stabilization" appears to take place even with a two-fold initial excess of  $B_2Cl_4$ . In this system, however, a definite reaction occurs:



with a half-time of about 5 days at room temperature to give the product we previously obtained<sup>8</sup> from the 1/1 addition:



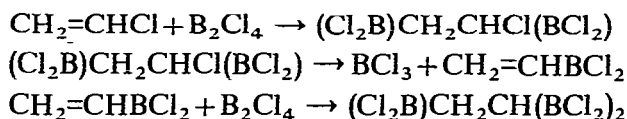
Formally, the reaction involves transfer of carbon-bonded halogen to boron with replacement of the C–Cl by a C– $BCl_2$  linkage and removal of unsaturation by addition of a molecule of  $B_2Cl_4$  across the double bond\*\*.

A plausible mechanistic pathway involves addition to the haloolefin followed by elimination of boron trichloride to yield dichlorovinylborane which, as previously

\* A preliminary account of portions of this work was given at the 156th National Meeting of the American Chemical Society, see ref. 12.

\*\* In a contract report<sup>13</sup>, Schlesinger and his co-workers have described a reaction of  $B_2Cl_4$  with excess vinyl chloride in which a portion of the olefin was consumed in five days and an equivalent amount of  $BCl_3$  was formed. Although the reaction products were not fully characterized, these workers may have observed the reaction described in the present work. Our own studies suggest, however, that the course of the reaction may be quite sensitive to the ratio of olefin to  $B_2Cl_4$  in the reaction mixture. From 1/2 mixtures of  $B_2Cl_4$  and  $C_2H_3Cl$ , the product, 1,1,2-tris(dichloroboryl)ethane is obtained reproducibly and in high yield. Mixtures of the reagents in 1/1 ratio, alone or in the presence of tetramethylsilane or mercury, produce a more complex set of products. While this 1/1 reaction has not been studied in detail, our preliminary evaluation, based on NMR observations and examination of cleavage products, suggests that the reaction products may include organoboron derivatives with organic groups containing more than two carbon atoms.

shown, will undergo rapid addition of a second molecule of  $B_2Cl_4$ :



In complete parallel to the behavior with vinyl chloride, reaction of  $B_2Cl_4$  with *trans*-2-chlorovinyl dichloroborane follows the same 2/1 stoichiometry to yield 1,1,2,2-tetrakis(dichloroboryl)ethane and  $BCl_3$ .

As a partial test of the mechanistic speculations above, we carried out several reactions in which the boron subhalide and the olefin contained different halogens in order to demonstrate further the transfer of halogen from carbon to boron. More complex product arrays were anticipated, since halogen redistribution is well known to occur between boron halides and organoboron halides<sup>14</sup>. In systems containing boron subhalides, the equilibrium halogen distribution may, however, be quite non-random<sup>15</sup>.

In the reactions of  $B_2Cl_4$  with vinyl bromide and 1-bromopropene, significant quantities of boron-bonded bromine were found in the products, which also included the expected 1,1,2-tris(dihaloboryl)alkanes. Somewhat surprisingly, the proton NMR spectra of the addition products were relatively simple. This suggests either that particular mixed halogen derivatives are favored or that the substitution of bromine for chlorine on boron produces only slight, unresolved effects on the chemical shifts of the protons on the organic groups. A third possibility is that we are observing the time average of several organoboron halides exchanging halogen rapidly on the NMR time scale.

In the vinyl bromide/ $B_2Cl_4$  system, we obtained NMR evidence (Fig. 1) for intermediate formation of a saturated species containing a  $>C(H)CH_2-$  group. Although the transient species was not sufficiently stable to permit total isolation, it was shown, upon removal of more volatile materials, to undergo decomposition with simultaneous formation of chlorobromoboranes and a species having a broad proton NMR peak in the olefinic region, whose hydrolysis chemistry indicated the presence of a vinyl group and boron-bonded halogen. We thus identify the intermediate as the product of initial addition to vinyl bromide, which can eliminate  $BCl_2Br$ , forming dihalovinylborane. A portion of the unsaturated organoborane undergoes subsequent addition of subhalide to yield a saturated product, analogous to that obtained with vinyl chloride, but containing both halogens.

Detection of the intermediate haloalkyldiboron compound in the reaction of  $B_2Cl_4$  with  $C_2H_3Br$  but not with  $C_2H_3Cl$  may be attributed to differences in relative rates of the steps in the suggested sequence. In the reaction of  $C_2H_3Cl$  with  $B_2F_4$ , which is much slower than the reaction with  $B_2Cl_4$ , only the ultimate, saturated product was detected, while in the  $C_2H_3Br/B_2F_4$  system, NMR and chemical evidence point to the accumulation of significant concentrations of a vinylboron intermediate in addition to the anticipated 1,1,2-tris(difluoroboryl)ethane. This suggests that the addition of  $B_2F_4$  to a vinylboron bromofluoride may be considerable less facile than the corresponding addition step in the  $C_2H_3Br/B_2Cl_4$  system, which is consistent with the generally lower reactivity of  $B_2F_4$  toward olefins as compared with  $B_2Cl_4$ <sup>2</sup>.

The reactivity of chloroolefins toward  $B_2Cl_4$  is markedly reduced by increased

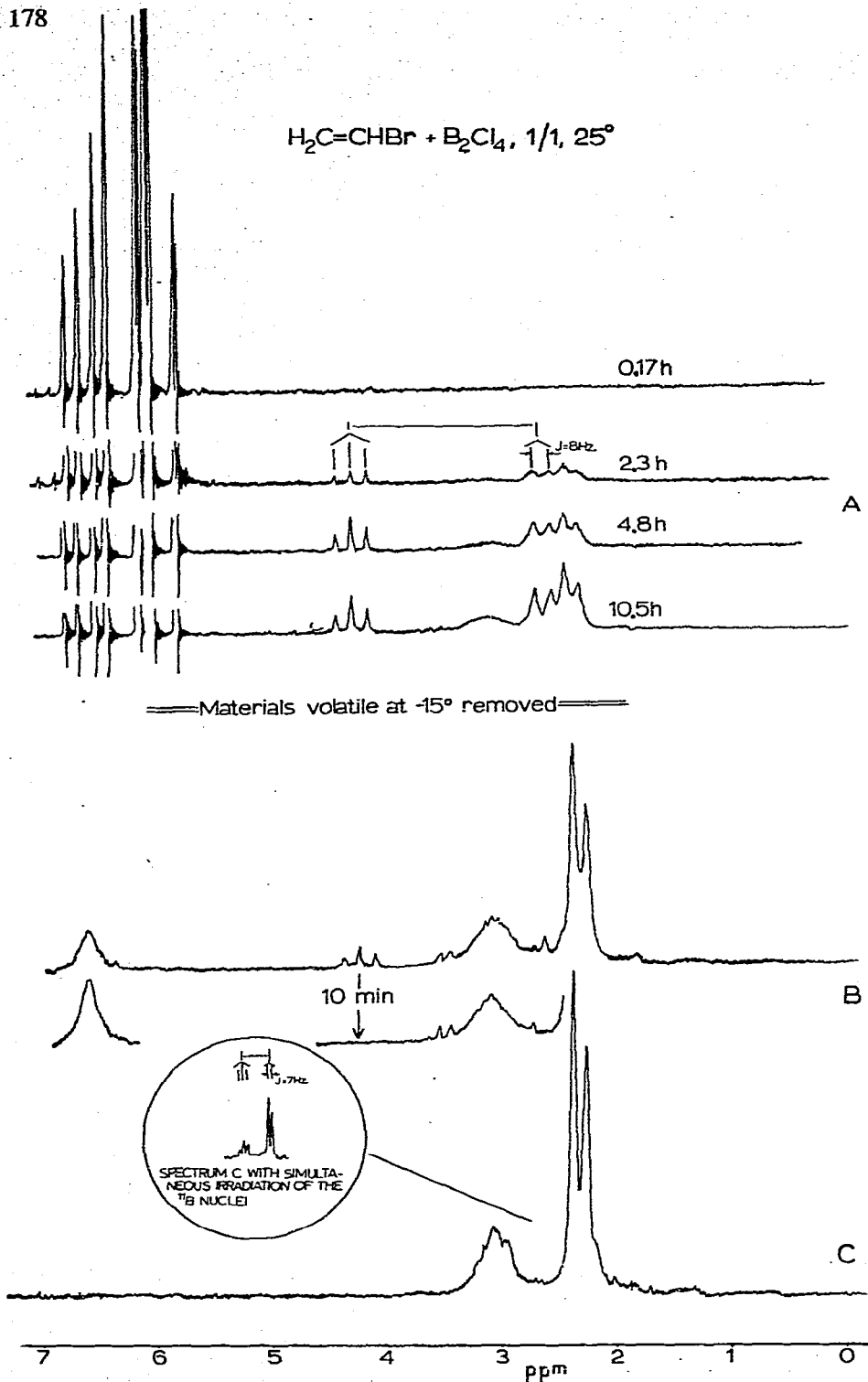


Fig. 1. Proton NMR spectra in the  $\text{B}_2\text{Cl}_4$ -vinyl bromide system: A. Spectra of the reaction mixture showing development of features in the high-field region. B. Spectra obtained following removal of materials volatile at  $-15^\circ$ , showing disappearance of triplet at  $\sim -4.2$  ppm and doublet at  $\sim -2.5$  ppm and growth of peak at  $-6.5$  ppm. C. Spectrum of isolated addition product. Inset shows effect of  $^{11}\text{B}$  decoupling.

chlorine substitution, and forcing conditions were required to produce significant reactions even in periods of weeks. Side reactions, possibly including both olefin polymerization and degradation of the subhalides, occurred under these conditions. In the case of the dichloroethylenes, no attempt was made to evaluate products in detail, although spectroscopic evidence indicated a similarity to the saturated polyboron products obtained in the vinyl halide reactions. Of particular interest was the appearance, at low levels, of the characteristic NMR spectrum of  $\text{ClCH}=\text{CHBCl}_2$  in reaction mixtures containing 1,2-dichloroethylenes, since this product would be expected as an intermediate in the sequence postulated above. The reaction of  $\text{B}_2\text{Cl}_4$  with  $\text{C}_2\text{HCl}_3$  appeared quite similar. Formation of  $\text{C}_2$ -fragments ( $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_3\text{Cl}$ ) on protonolysis is consistent with the formation of  $\text{C}_2$ -organoboron species and suggests that the involatile products are polyboryl compounds rather than mere polymerization products of the starting olefin.

#### EXPERIMENTAL

The high-vacuum techniques and inert atmosphere procedures used in handling the air-sensitive materials encountered in this work have been described previously<sup>8,15</sup>.

Many of the reactions were carried out in sealed NMR tubes which permitted continuous monitoring of the reactions. Tetramethylsilane was generally omitted as an internal standard due to the known reactivity of  $(\text{H}_3\text{C})_4\text{Si}$  with  $\text{B}_2\text{Cl}_4$ <sup>16</sup>. Chemical shifts were estimated by substituting a tube of pure  $(\text{H}_3\text{C})_4\text{Si}$  for the sample immediately before and after the sample spectrum had been obtained. The reaction tubes were ultimately opened into the vacuum system, and the volatile contents removed for subsequent evaluation.

Elemental analyses were performed by commercial laboratories and by the Analytical Chemistry Division of the National Bureau of Standards.

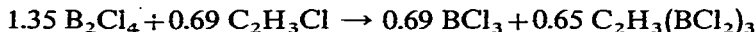
#### Reagents

The boron subhalides were prepared and purified as in our previous work<sup>8</sup>. The halocarbons were obtained commercially and purified as follows: *cis*- and *trans*- $\text{H}_2\text{C}_2\text{Cl}_2$  were obtained as pure isomers by a gas chromatographic separation on 20 wt. % silicone oil on 60 to 80 mesh firebrick at 25°. The  $\text{HC}_2\text{Cl}_3$  was stored under 1 atm  $\text{BCl}_3$  for 3 days and subsequently separated from the  $\text{BCl}_3$  by repeated trap to trap fractionations. The  $\text{H}_3\text{C}_2\text{Cl}$ ,  $\text{H}_3\text{C}_2\text{Br}$ ,  $\text{H}_2\text{C}_2\text{Cl}_2$ ,  $\text{C}_3\text{H}_5\text{Br}$ , and  $\text{C}_2\text{H}_5\text{Cl}$  were subjected to appropriate trap to trap fractionation. The *n*-hexane was distilled from  $\text{LiAlH}_4$  under dry nitrogen. The purity of each material was judged from a comparison of its infrared spectrum to that of an authentic sample of the same material.

#### Reaction of $\text{B}_2\text{Cl}_4$ with vinyl chloride

Vinyl chloride (2.41 mmol) and  $\text{B}_2\text{Cl}_4$  (4.92 mmol) were combined in a 10 ml borosilicate glass reaction vessel closed with a glass-polytetrafluoroethylene stopcock and held at room temperature for four days. The resulting clear, colorless mixture was fractionated in the vacuum line through traps held at  $-63$  and  $-96$  into a  $-196^\circ$  trap. The  $-196^\circ$  fraction consisted of 2.41 mmol of a mixture of  $\text{BCl}_3$  and  $\text{C}_2\text{H}_3\text{Cl}$  which, upon treatment with water, gave 1.72 mmol  $\text{C}_2\text{H}_3\text{Cl}$ . The  $-96^\circ$  fraction contained 3.57 mmol of unreacted  $\text{B}_2\text{Cl}_4$ , while the  $-63^\circ$  fraction gave 175 mg (0.65 mmol)

of a clear oil shown by infrared and proton magnetic resonance spectroscopy to be 1,1,2-tris(dichloroboryl)ethane, identical to the material obtained by 1/1 reaction of  $B_2Cl_4$  with  $C_2H_3BCl_2$ . The net reaction was thus:



about 30% of the vinyl chloride being consumed in four days. In similar experiments, reaction mixtures ( $B_2Cl_4/C_2H_3Cl=2/1$ ) were prepared in two NMR tubes, one of which was kept ca. 11 cm from two continuously operated 40 W fluorescent lamps while the other was kept dark except for brief periods during which the NMR spectrum was examined. Measurement of peak integrals indicated that half of the olefinic starting material in each tube was converted to the saturated product in about five days. No significant effect of light on the reaction was noted under these conditions.

#### *Reaction of $B_2Cl_4$ with trans-2-chlorovinyl dichloroborane*

In preliminary NMR investigations of 1/1 reactions in this system, weak absorptions were noted at  $-3.6$  and  $-6.8$  ppm after about seven days at room temperature. Over the next thirty days, the signal at  $-6.8$  ppm remained essentially constant in intensity. The broad peak at  $-3.6$  ppm increased, while the AB pattern of the starting vinylborane diminished correspondingly.

In a preparative scale experiment,  $B_2Cl_4$  (4.38 mmol) and  $ClC_2H_2BCl_2$  (4.38 mmol) were held at room temperature for 82 days. Fractionation of the product mixture gave 0.23 mmol HCl, 2.41 mmol  $BCl_3$ , and 306.1 mg of a mixture of  $B_2Cl_4$  and  $ClC_2H_2BCl_2$  which, on heating with 12% aqueous NaOH at  $105^\circ$  for 18 h, gave 0.02 mmol  $H_2$ , indicating the presence of a like amount of unreacted  $B_2Cl_4$ . The remaining product was a white solid, m.p.  $32-35^\circ$ , whose IR and proton NMR spectra were identical to those of 1,1,2,2-tetrakis(dichloroboryl)ethane, prepared from  $C_2H_2$  and  $B_2Cl_4$  by the method of Chambers *et al.*<sup>4</sup>. The molecular weight and elemental analyses confirmed the formulation as  $C_2H_2(BCl_2)_4$ . (Found: C, 7.32; H, 0.67; B, 13.06; Cl, 77.8; mol.wt., 341.  $C_2H_2B_4Cl_8$  calcd.: C, 6.81; H, 0.57; B, 12.2; Cl, 80.4%; mol.wt., 354.)

#### *Reaction of $B_2Cl_4$ with vinyl bromide*

Reaction of  $B_2Cl_4$  (3.18 mmol) with  $C_2H_3Br$  (1.59 mmol) at room temperature for 21 days yielded 1.74 mmol of mixed chlorobromoboranes containing 4.87 and 0.39 mmol of hydrolyzable chloride and bromide respectively. The principal product was a clear, relatively volatile oil which gave 7.24 mmol chloride and 0.80 mmol bromide on alkaline hydrolysis. On the basis of volatility and by analogy to the vinyl chloride system, this product was tentatively formulated as a tris(dihaloboryl)ethane, accounting for 1.34 mmol of the original olefin. A small amount of involatile, light yellow oil remained in the reaction bulb. This experiment demonstrated unequivocally the transfer of carbon-bonded bromine to boron in the course of the reaction.

In another experiment, 2.90 mmol of each reagent were combined in an NMR sample tube which was sealed, maintained at  $25^\circ$ , and examined periodically by proton NMR. After 10.5 h, the spectrum showed four distinct new features (Fig. 1) in addition to the spectrum of vinyl bromide: a triplet with a splitting of  $\sim 8$  Hz at  $-4.2$  ppm, a doublet of the same splitting at  $-2.5$  ppm, a broad peak centered at ca.  $-3$  ppm, and a second doublet (7 Hz) at  $-2.2$  ppm. The tube was quenched in liquid nitrogen, opened

to the vacuum line, and warmed over 2.5 h with a succession of baths at  $-80$ ,  $-35$ , and  $-15^\circ$  while volatiles were distilled off. The volatiles consisted of 2.62 mmol of a mixture of boron chlorobromides and  $C_2H_3Br$  from which 1.14 mmol of the bromolefin was recovered after treatment with distilled water. The tube was then resealed and inserted into the spectrometer. The spectrum showed that all the  $C_2H_3Br$  had been removed. The other resonances previously observed remained, although the  $-2.2$  ppm doublet and the  $-3$  ppm peak had increased relative to the two other features, and a new, broad absorption suggestive of an organoboron compound had appeared in the olefinic region at  $-6.5$  ppm. After 10 min, the olefinic peak had increased further, while the triplet and the  $-2.4$  ppm doublet had disappeared.

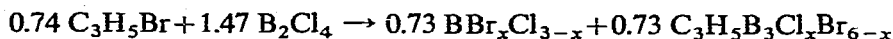
Fractionation of the tube contents gave a clear light yellow liquid, (A), retained at  $-80^\circ$ , and a more volatile mixture of boron chlorobromides and a second liquid, (B), along with some HCl. The proton NMR spectrum of the isolated product (A) was essentially identical to the high-field portion of the spectrum that had been seen in the reaction mixture after disappearance of the 8 Hz doublet and triplet. By the use of  $^{11}B$  decoupling, the spectrum was resolved into a triplet and doublet with 1/2 intensity ratio, indicating the presence of an organoboron compound containing a  $\text{>C(H)CH}_2\text{-}$  grouping.

Separation of the components of the volatile fraction on a low temperature column gave 0.37 mmol HCl, 0.48 mmol of boron chlorobromides, and 0.47 mmol of (B), which showed strong IR bands at 1605, 915, and  $870\text{ cm}^{-1}$ . A portion of (B) was heated with  $CH_3COOH$  at  $100^\circ$  for 16 h, producing  $CH_3COCl$ ,  $C_2H_4$ , and HCl. A second portion was hydrolyzed with dilute aqueous base, and the resultant solution was analyzed for halide, indicating a Cl/Br ratio of 8.5. It thus appeared that (B) was a mixture of vinylboron chlorobromides, principally  $C_2H_3BCl_2$ , formed along with the boron bromochlorides, by decomposition of a precursor following removal of vinyl bromide from the reaction mixture. Since the development of the proton resonance intensity in the olefinic region was accompanied by the disappearance of the 8 Hz triplet/doublet system at higher field, we may infer with some confidence that the transitory spectrum is that of the precursor and that this also contains a  $\text{>C(H)-CH}_2\text{-}$  grouping.

#### *Reaction of $B_2Cl_4$ with 1-bromopropene*

A 1/1 reaction (1.47 mmol of each reagent) of  $B_2Cl_4$  with  $C_3H_5Br$  (ca. 80% *cis* isomer) was carried out at room temperature in an NMR tube. The spectrum showed the usual diminution of the olefin and the appearance of product peaks, together with a transient doublet at  $-3.8$  ppm which disappeared from the spectrum after 4.5 h. After 10.5 h, the reaction mixture was found to contain 0.73 mmol of chloroboroboranes, 0.73 mmol of unreacted 1-bromopropene, 217 mg of a clear oil that was retained in a  $-35^\circ$  trap during the fractionation, and 0.17 mmol of a mixture (ca. 1/1) of HCl and HBr. The product had significant IR absorptions at 2960, 2860, 1620, 1460, 925, 910, 860, 825, 650, and  $590\text{ cm}^{-1}$ . The proton NMR spectrum showed a broad resonance at  $-2.8$  ppm and a doublet at  $-1.1$  ppm (intensities 2.05/3.00). Treatment of a portion of this material with propionic acid gave propionyl chloride, HCl, and propane. The spectroscopic properties, mass balance, and formation of propane on protonolysis are in accord with formulation of the product as a tris(dihaloboryl)propane or a mixture of such compounds containing both halogens. Boron and hy-

drocarbon balances are consistent with reaction according to:



#### *Reaction of B<sub>2</sub>F<sub>4</sub> with vinyl chloride*

Vinyl chloride (2.59 mmol) and B<sub>2</sub>F<sub>4</sub> (2.61 mmol) were combined in an NMR tube and held at room temperature for a period of about 6 months, during which the spectrum was examined periodically. During this period, a broad absorption appeared at *ca.* -1.1 ppm and a red color developed in the sample tube. Fractionation of the tube contents indicated that both reagents had been consumed. The product fraction passing -130° consisted of 1.59 mmol BF<sub>3</sub> and 0.2 mmol HCl. Material distilling from the reaction tube and retained at -130° consisted of 180 mg of a clear oil. The IR spectrum of the vapor over this material was identical with that of 1,1,2-tris(difluoroboryl)ethane, as was the proton NMR spectrum. Treating this product with propionic acid at 125° for 2 days gave the expected ethane and SiF<sub>4</sub>, along with some propionyl chloride and HCl, indicating the presence of some boron-bonded chlorine in the product. An involatile air-sensitive red oil remained in the sample tube after removal of the volatiles.

#### *Reaction of B<sub>2</sub>F<sub>4</sub> with vinyl bromide*

Vinyl bromide (1.51 mmol) was allowed to react with B<sub>2</sub>F<sub>4</sub> (1.52 mmol) at room temperature for 37 days, during which time broad resonances developed in the proton NMR spectrum at -1.1 ppm and in the olefinic region at -6.3 ppm. Separation of the reaction mixture gave 1.07 mmol BF<sub>3</sub>, 0.27 mmol HBr, 0.62 mmol of unreacted C<sub>2</sub>H<sub>3</sub>Br and two less volatile products. The first of these, which passed a trap at -63° and was retained at -85°, consisted of 0.24 mmol of a material whose infrared spectrum was consistent with the presence of vinyl, B-Br, and B-F groupings. Hydrolysis of a portion of this material with dilute aqueous base and analysis of the resulting solution gave a F/Br ratio of 1.01/1. Treatment of a 0.09 mmol of the fraction with acetic acid for 16 h at 100° gave 0.087 mmol of ethylene and 0.033 mmol of CH<sub>3</sub>-COBr. This material was thus formulated as a vinylboron bromofluoride or a mixture of C<sub>2</sub>H<sub>3</sub>BF<sub>2</sub> with C<sub>2</sub>H<sub>3</sub>BBr<sub>2</sub>.

The second product, retained at -63°, was 0.34 mmol of a material with an infrared spectrum identical to that of 1,1,2-tris(difluoroboryl)ethane and a molecular weight (vapor density) of 178 (C<sub>2</sub>H<sub>3</sub>B<sub>3</sub>F<sub>6</sub> calcd.: 173.4).

#### *Reactions of B<sub>2</sub>Cl<sub>4</sub> with polychloroethylenes*

These reactions were much slower than the corresponding reactions of vinyl chloride, and investigations were confined principally to NMR observations.

*cis*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>. A sample tube containing 2.70 mmol each of the olefin and B<sub>2</sub>Cl<sub>4</sub> was maintained at 100° for 10 weeks. A broad peak slowly developed in the proton NMR spectrum at -3.6 ppm, indicating formation of a saturated product. Small absorptions also appeared between -6.5 and -8.2 ppm, and the colorless mixture turned orange. At the end of 10 weeks, the resonance at -3.6 ppm accounted for *ca.* 23% of the total signal intensity. Of particular interest was the appearance in the low-field region of a weak four line AB pattern. Examination of this region at 220 MHz clearly showed the existence of two pairs of doublets split by 14.8 Hz with a separation of 223.5 Hz. These parameters agree with those calculated for *trans*-2-chlorovinyl-



dichloroborane at 220 MHz. From comparison with the intensity of the outer  $^{13}\text{C}$  satellite doublet of the dichloroethylene [ $J(\text{HH})$  5.4 Hz], the material giving rise to the AB pattern was estimated to account for *ca.* 0.5% of the total proton intensity in the sample.

*trans-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>*. The behavior of this system was essentially identical to that of the system containing the *cis* isomer. After 10 weeks at 100°, the spectrum showed a broad resonance at -3.6 ppm (31% of total intensity) and additional signals at low field. The 220 MHz spectrum revealed the same AB pattern found in the reaction of *cis*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>. Comparison with the outer satellite doublets [ $J(\text{HH})$  12.1 Hz] of the dichloroethylene indicated that the compound giving rise to the AB pattern comprised 4% of the sample.

*1,1-Dichloroethylene*. A 1/1 mixture (3.26 mmol of each component) formed a dark green precipitate within 18 h at room temperature. Over a period of 8 months at room temperature, a broad proton signal developed at -2.6 ppm, and a narrower peak at -2.7 ppm. Separation of the mixture gave HCl, 2.12 mmol unreacted olefin, and 2.39 mmol of BCl<sub>3</sub> containing about 8% B<sub>2</sub>Cl<sub>4</sub>. Some 210 mg of a clear oil giving a broad NMR signal at -2.7 ppm with singlet  $^{13}\text{C}$  satellites [ $J(\text{CH})$  116 Hz] were obtained in a -35° trap. A light brown residue remained in the tube. The IR spectrum of the product showed (saturated) C-H stretching bands, and bands in the B-Cl stretching region.

*Trichloroethylene*. A mixture of 0.87 mmol C<sub>2</sub>HCl<sub>3</sub> and 2.78 mmol B<sub>2</sub>Cl<sub>4</sub> was maintained at 105° for 3 months, during which time a yellow color developed. At the end of this period, the NMR signal of C<sub>2</sub>HCl<sub>3</sub> (-6.28 ppm) had disappeared, and several broad, weak resonances had appeared in the region from -2 to -4 ppm. The reaction mixture was fractionated to yield 0.19 mmol HCl, 2.70 mmol of a mixture of B<sub>2</sub>Cl<sub>4</sub> and BCl<sub>3</sub> from which 0.23 mmol H<sub>2</sub> was produced on alkaline hydrolysis, a yellow oil that distilled from the reaction tube into a -80° trap, and a viscous involatile residue. The -80° fraction liberated both ethane and vinyl chloride on treatment with propionic acid, while only ethane was obtained from similar treatment of the involatile residue.

#### *Decomposition of B<sub>2</sub>Cl<sub>4</sub> in inert solvents*

Mixtures of B<sub>2</sub>Cl<sub>4</sub> (1.61 mmol) with *n*-C<sub>6</sub>H<sub>14</sub> (3.24 mmol) and of B<sub>2</sub>Cl<sub>4</sub> (1.59 mmol) with C<sub>2</sub>H<sub>5</sub>Cl (3.20 mmol) were sealed into 10 ml glass reaction bulbs and held at room temperature for 6 days. Both systems developed red precipitates during this interval. In both systems, the solvent was recovered quantitatively at the end of the reaction. Measurement of hydrogen produced on hydrolysis with aqueous base indicated that 1.44 mmol (89.4%) of B<sub>2</sub>Cl<sub>4</sub> remained in the hexane system and 1.47 mmol (92.5%) in the ethyl chloride system after the six day reaction time.

#### ACKNOWLEDGEMENTS

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